

THE NATURE OF THE REACTION INTERMEDIATE IN METHANATION BY IRON CATALYST

Hiroshige MATSUMOTO

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Abstract

In the reduction of carbon monoxide with hydrogen to methane on a commercial iron catalyst, a transient method was used to study the reaction intermediates at 250°C and atmospheric pressure. When a stream of the reactant mixture (10% carbon monoxide in hydrogen) flowing over the catalyst in a steady state was suddenly changed to pure hydrogen, a surface intermediate was converted to methane at a rate higher than that at the steady state. The intermediate species was deactivated by a similar sudden change to helium. Since the amount of the reaction intermediate deactivated by the inert gas treatment corresponded to the amount of water removed from the surface during the inert gas treatment, this deactivation process was explained by the assumption that an intermediate of enol type on the iron was dehydrated to an inactive carbon species. The reactivity of the enol reaction intermediate was much higher than carbon deposited on the surface.

Introduction

The steady-state flow method has been widely used in the kinetic study of Fischer-Tropsch and related syntheses. Careful measurements on many catalysts have been made by Vannice (1) and Dalla Betta et. al. (2) by means of this method. Recently the transient response method has been developed for heterogeneous catalysis, and recent reviews (3) and work (4) well describe the principle and the applicability of this method.

Here we have used the transient method to study the reduction of carbon monoxide with hydrogen. One of the objectives of the present work is to get information which is difficult to obtain by the conventional flow method. When a stream of the reactant mixture (carbon monoxide and hydrogen) flowing to the catalyst at steady state is suddenly changed to pure hydrogen or helium, a different composition of reaction products can be expected in the outlet gas stream. Analysis of this phenomenon permits obtaining information concerning intermediate species on the catalyst at steady state.

The mechanisms for the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen have been the subject of much speculation and experiment because of the complexity of the reaction. The earliest theory of the reaction was the carbide theory

(5). Metal carbonyls (6) and methylene radicals (7) were also proposed as the reaction intermediates. Recently Wise and co-workers (8) and Araki and Ponc (9) suggested a surface carbon species as an intermediate for methanation on a nickel catalyst. Another well-known idea is that an adsorbed complex of formula HCOH is formed during hydrocarbon synthesis. This theory was proposed by Storch, Golumbic and Anderson (10) and modified by Kummer and Emmett (11) and by Hall et. al (12).

Experimental

The transient experiment was performed at 250C under atmospheric pressure. The schematic diagram of the apparatus used is shown in Fig. 1. A stream of gas to the reactor was switched to another by a 4-way valve. The needle valves were carefully adjusted so that this switch did not alter the pressure in the reactor or the flow rate measured by the soap-bubble flowmeter. The analysis of the reactants and products was carried out by a mass spectrometer. The mass spectrometer was suitably calibrated by known pure gases and gas mixture for each run so as to take account of the cracking patterns. The continuous inlet system to the mass spectrometer has a response time sufficiently small to permit good resolution of the inlet step function. The tubular reactor made from stainless steel was held in an electronically controlled furnace of large heat capacity to keep the temperature constant. The maximum variation of temperature over the reactor was less than 1C. 50 mg of the catalyst was held between

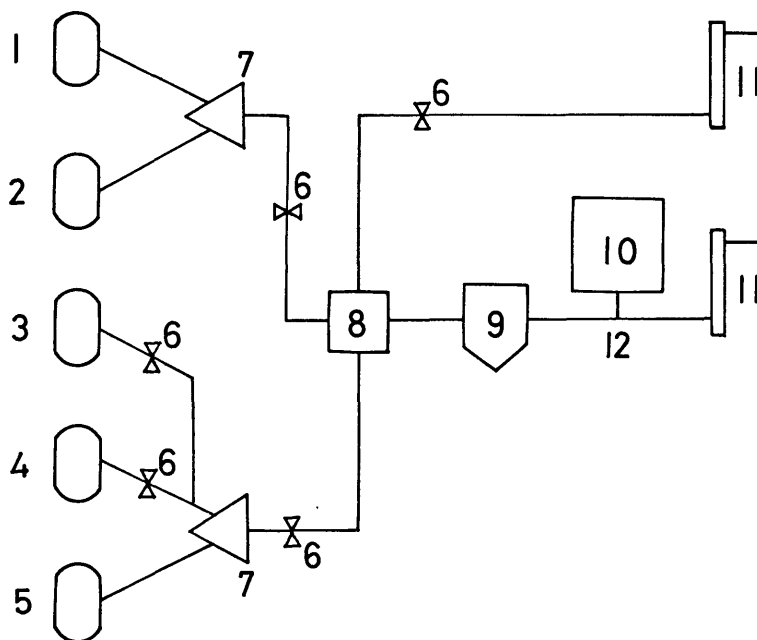


Fig. 1. Schematic diagram of equipment used for transient experiments. 1, 2, 3, 4, and 5, high pressure cylinders for hydrogen, helium, argon, carbon monoxide and 10% carbon monoxide in hydrogen, respectively; 6, needle valves; 7, 3-way switching valve; 8, 4-way switching valve; 9, reactor; 10, mass spectrometer; 11, flowmeters; 12 heating tape.

silica beads to minimize the dead volume of the reactor. The silica beads and the stainless reactor were confirmed to be inactive for the reaction.

The iron catalyst used in the present work was CCI fused magnetite catalyst with the composition: Fe_3O_4 , 96.5%; Al_2O_3 , 2.5%; K_2O , 0.6% and SiO_2 , 0.4%. The catalyst was reduced in a hydrogen stream for a period of 48 hr at 450C before use. The surface area of the reduced catalyst was determined to be 13.0 m^2/g by the BET method. The particle size of the catalyst used ranged from 250 to 300 μm . The reaction mixture was 10.02% carbon monoxide in hydrogen. The gases used in this experiment have no peak of mass number 32 in the mass spectrum.

Carbon-covered catalyst was prepared by the disproportionation reaction of 2.0% carbon monoxide in helium, yielding surface carbon and carbon dioxide at 250 C under atmospheric pressure. The amount of carbon deposited on the surface was determined from the amounts of carbon monoxide consumed during certain periods of the reaction. During the periods of 1, 5, 10, 20, 40 and 70 min, 0.13, 0.25, 0.36, 0.54, 0.88 and 1.39 mmole/g of carbon, respectively, were deposited on the surface of the iron catalyst.

Results

The freshly reduced catalyst took approximately 60 minutes to attain a steady state for the formation of methane, water and carbon dioxide. After the catalyst was reduced with hydrogen for 48 hr at 450C, the system was cooled down to the reaction temperature, 250C, in a hydrogen stream. Prior to exposure to the carbon monoxide-hydrogen mixture, the catalyst was treated with helium for 1 hr at 250C to remove the adsorbed hydrogen. On the introduction of the reaction mixture to the pretreated catalyst at a flow rate of 390 cc/min.g, immediate formation of water and carbon dioxide were observed in the outlet gas, as shown in Fig. 2. These formation rates decreased slowly

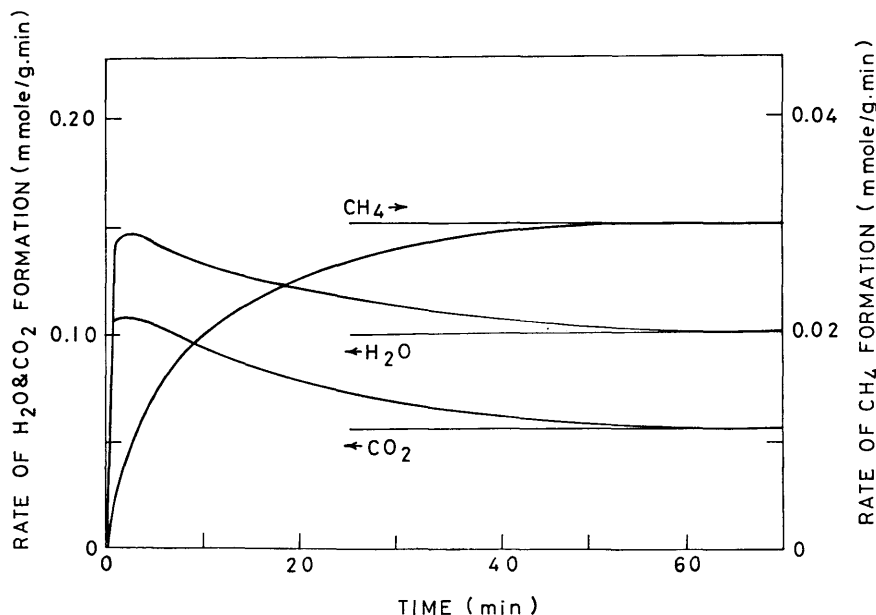


Fig. 2. Formation of major components as a function of exposure.

with the time on stream and reached steady state values after 1 hr. On the other hand, the methane formation rate increased gradually with the time to reach steady state also after 1 hr. These periods required to get to steady values depended on the composition of the reactant and on the reaction temperature. The processes occurring during these transients will be discussed in a separate paper.

The computation of reaction rates from observed transient data is much simplified by the low concentrations used in the differential reactor. The corresponding high gas velocity through the bed and the small particle size insure that there are no transport limitations. For a differential reactor the mass balance for a component j not present in the feed is:

$$\frac{d\bar{C}_j}{dt} = \bar{r} - \frac{C_j}{\theta} \quad (1)$$

where θ = residence time V/q , min.

V = void volume of reactor

q = flow rate, ml/min.

C_j = outlet concentration of j , mole/ml

\bar{C}_j = average C_j in the reactor, mole/ml

\bar{r} = reaction rate, mole/min (ml)

For all data reported here, $\theta = 4 \times 10^{-4}$ min, C_j for methane is typically 5×10^{-8} mole/ml, and $d\bar{C}_j/dt$ is never more than 10^{-7} mole/min(ml). Thus the derivative is negligible, and it is sufficiently accurate to report rates calculated by the equation:

$$\bar{r} = C_j / \theta \quad (2)$$

or

$$r = C_j q / w \quad (3)$$

in mmole/min (g), where W is g of magnetite.

When the stream of the reaction mixture flowing to the catalyst in the steady state was suddenly changed to pure hydrogen at the same flow rate, immediate formation of a large amount of methane was observed. The methane formation rate rapidly decreased with the time on stream of hydrogen, and then reached a constant value of 0.002 mmole/g. min within 1 hr, as shown in Fig. 3. During the course of the hydrogen flushing the only major component other than methane was water, although small amounts of higher hydrocarbons, such as ethane and propane, were observed at the beginning of the flushing.

When the catalyst in the steady state was exposed to a pure helium stream, neither methane nor carbon dioxide was observed, but an appreciable amount of water was detected in the outlet helium stream. After a certain period of the helium flushing, the feed to the reactor was switched to hydrogen. An appreciable amount of methane was formed on this introduction of hydrogen; small quantities of ethane and propane were also observed.

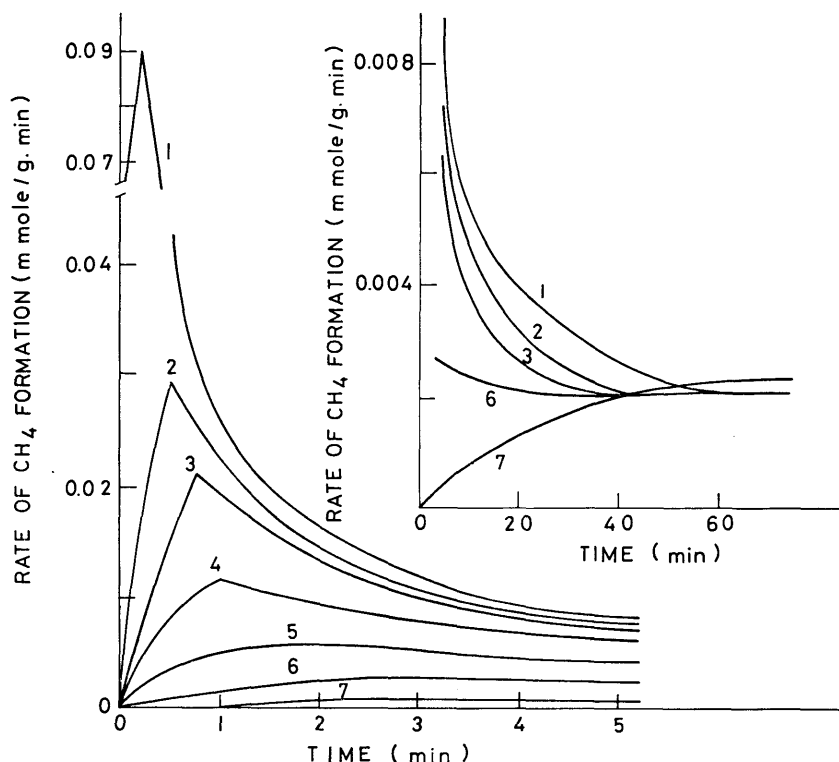


Fig. 3. Methane formation by hydrogen flushing of the steady-state catalyst after various helium treatments. Helium treatment: (1) 0 min; (2) 1 min; (3) 5 min; (4) 30 min; (5) 90 min; (6) 270 min; (7) 1080 min.

The results are shown in Fig. 3 for various periods of the helium treatment. The formation rate of methane was found to increase first and then decrease with the time on stream of hydrogen. The time for the maximum methane formation rate increased with increase of the period of helium treatment. The catalyst treated by helium over night showed no such point. For all the catalysts with various treatments the same steady formation rate of methane was observed as after 1 hr of hydrogen flushing. This constant value of methane formation rate was 0.002 mmole/g. min. After this condition was obtained, the temperature was elevated from 250 to 450°C at a rate of about 10°C/min in the hydrogen. The rate of methane formation strongly increased with the temperature and the maximum formation rate was observed at approximately 400°C. The total amount of methane formation by hydrogen flushing at both temperatures was estimated to be 5.7 mmole/g, which was independent of the period of the helium treatment within experimental error. It might be considered that at least two kinds of surface intermediates exist on the iron catalyst in the steady state. One is reduced to methane by hydrogen with an appreciable rate at 250°C. This type of species is deactivated on the surface by helium flushing, since no appreciable amount of carbonous compound was observed in the gas phase during the helium treatment. The other is slowly converted to methane by hydrogen. This type of species is not removed or deactivated even by overnight helium treatment.

If it can be postulated the former species acts as the reaction intermediate determining the actual rate of methane formation at steady state, the rate of hydrogenation of the intermediate can be determined from the results shown in Fig. 3 assuming a first order dependence of the rate on the amount of the intermediate. For surface species X reacting to methane, Eq. (1) becomes

$$\frac{d[X]}{dt} = r \quad (4)$$

and Eq. (3) holds for methane, written as

$$r = \frac{q}{W} [CH_4] \quad (5)$$

where $[X]$ and $[CH_4]$ are the amount of the intermediate on the surface and that of methane formed from the intermediate, respectively. Thus $d[X]/dt$ is measured by the rate of methane formation, as reported on Fig. 3. The accumulated methane formed is $[CH_4]_t$, found from $\int_0^t r dt$, the area under a curve of Fig. 3. Thus the amount of intermediate is given by:

$$[X]_t = [X]_0 - [CH_4]_t \quad (6)$$

If surface hydrogen is kept at a high concentration by the hydrogen flushing, the rate of hydrogenation of X should be first order in X:

$$-\frac{d[X]}{dt} = k[X] \quad (7)$$

Integration yields

$$\ln[X]_0 - \ln[X]_t = kt \quad (8)$$

and

$$\ln \{ [X]_0 - [CH_4]_t \} = \ln[X]_0 - kt \quad (9)$$

where $[X]_0$ and $[X]_t$ represent the amount of the intermediate on the surface before hydrogen flushing and after t minutes in hydrogen, respectively. According to the previous discussion, $[X]_0$ for each catalyst can be determined by the subtraction of the total amount of methane formed within 1 hr at 250C for the catalyst treated by helium over night from that for each catalyst with the various helium treatments. Furthermore, $[CH_4]_t$ can be estimated also from the difference in the amount of methane formed over the catalyst with various helium treatments and that formed over the catalyst with overnight helium treatment. The logarithms of $\{ [X]_0 - [CH_4]_t \}$ are plotted against the time in Fig. 4 according to Eq. (9). The data show good linear relationships which have practically the same slopes.

An appreciable amount of water was detected instantaneously on the introduction of helium to the catalyst in the steady state, although neither methane nor carbon dioxide was observed during this period. The amount of water formation during the helium flushing is shown in Fig. 5, along with that during the hydrogen flushing. On the introduction of helium to the catalyst in the steady state at 250C, the peak corresponding to mass number 18 decreased rapidly at first and then slowly after 70 minutes the water formation almost ceased. The amount of water formed in this stage was estimated to be 0.18 mmole/g. At this point the temperature was elevated in the helium to 450C

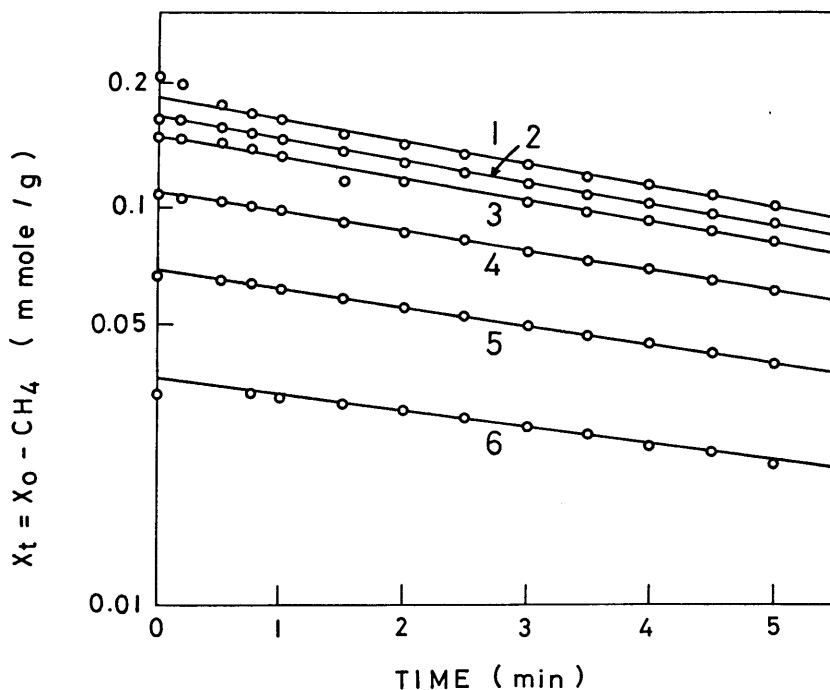


Fig. 4. First-order dependence of methane formation from the intermediate on the steady-state catalyst after various helium treatments. Helium treatment: (1) 1 min; (2) 5 min; (3) 30 min; (4) 90 min; (5) 270 min; (6) 1080 min.

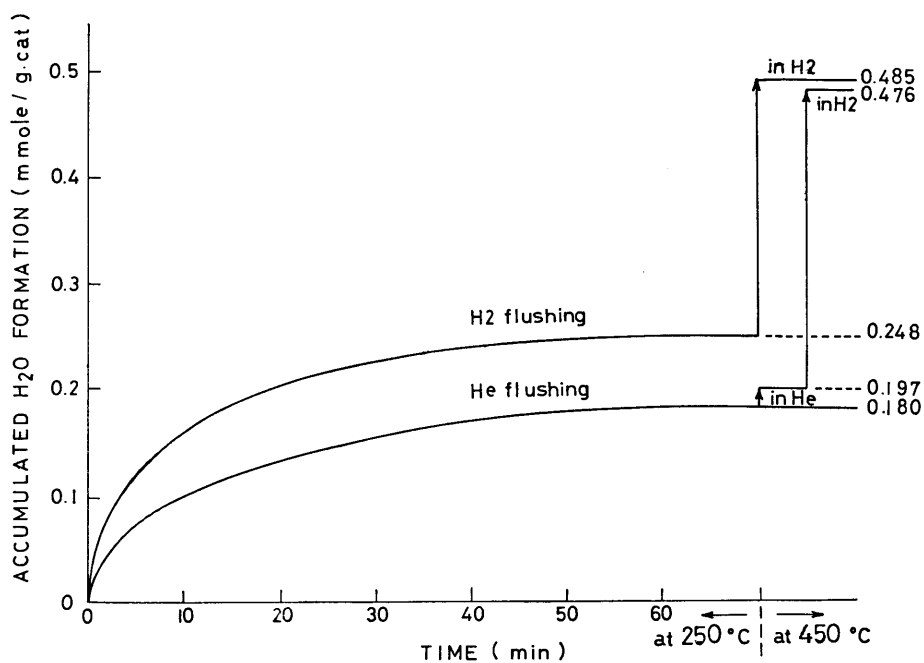


Fig. 5. Amount of water removed from the steady-state catalyst by helium and hydrogen flushing.

where only 0.017 mmole/g of water was formed. When the stream of helium flowing to the reactor was changed to hydrogen at 450C, further formation of water (0.29 mmole/g) was found at an appreciable rate. If hydrogen flushing was carried out in the similar way to the helium flushing, 0.248 and 0.237 mmole/g of water were formed at 250 and 450C, respectively. There is no appreciable difference in the total water formation between the first run (0.476 mmole/a) and the second run (0.485 mmole/g). The difference in the water formation at 250C between by helium and hydrogen flushing is presumably due to the removal of surface oxygen and hydroxyl groups by hydrogen.

The results calculated from the data in Figs. 3, 4, and 5 are summarized in Table 1. The amount of methane formed by hydrogen flushing at 250C decreased with the period of helium flushing. The calculated amount of the intermediate species which was deactivated by the helium treatment increased with the period of the treatment. Furthermore, the rate constant for methane formation from the intermediate, which was calculated from the slopes of plots in Fig. 4, was substantially independent of the helium treatment and was estimated to be 0.12 minute.⁻¹

Table 1 Influence of Helium Treatment on Surface Intermediate

He treatment (min)	CH ₄ formed within 65 min (mmole/g)	X on the surface (mmole/g)	X deactivated by He (mmole/g)	H ₂ O removed by He (mmole/g)	k for CH ₄ from X (min ⁻¹)
0	0.31	0.20	0	0	0.12
1	0.26	0.15	0.05	0.03	0.12
5	0.25	0.14	0.06	0.07	0.12
30	0.19	0.10	0.10	0.15	0.12
90	0.16	0.05	0.15	...	0.11
270	0.14	0.03	0.17	...	0.11
1080	0.11	0	0.20	0.20	...

Discussion

Since the rate constant for methane formation from the reaction intermediate X was independent of the amount of X on the surface (Fig. 4 and Table 1), it may be considered that the intermediate is only one kind of chemical entity. Furthermore, the amount of X deactivated by helium flushing substantially corresponded to the amount of water removed from the surface during the helium flushing (Table 1). From these points of view, an adequate structure of the intermediate species X seems to be the enol form. Thus, the following dehydration reaction might be considered for the deactivation process by the inert gas treatment:

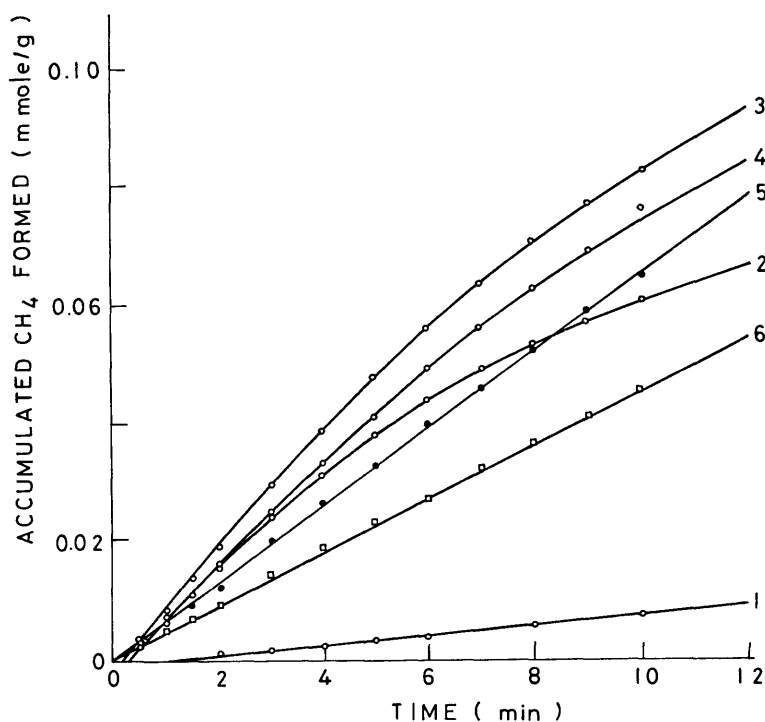


Fig. 6. Amount of methane formed by hydrogen flushing the catalyst covered by various amount of carbon at 250C. Amount of surface carbon: (1) 0.13 mmole/g; (2) 0.25 mmole/g; (3) 0.36 mmole/g; (4) 0.54 mmole/g; (5) 0.88 mmole/g; (6) 1.39 mmole/g.

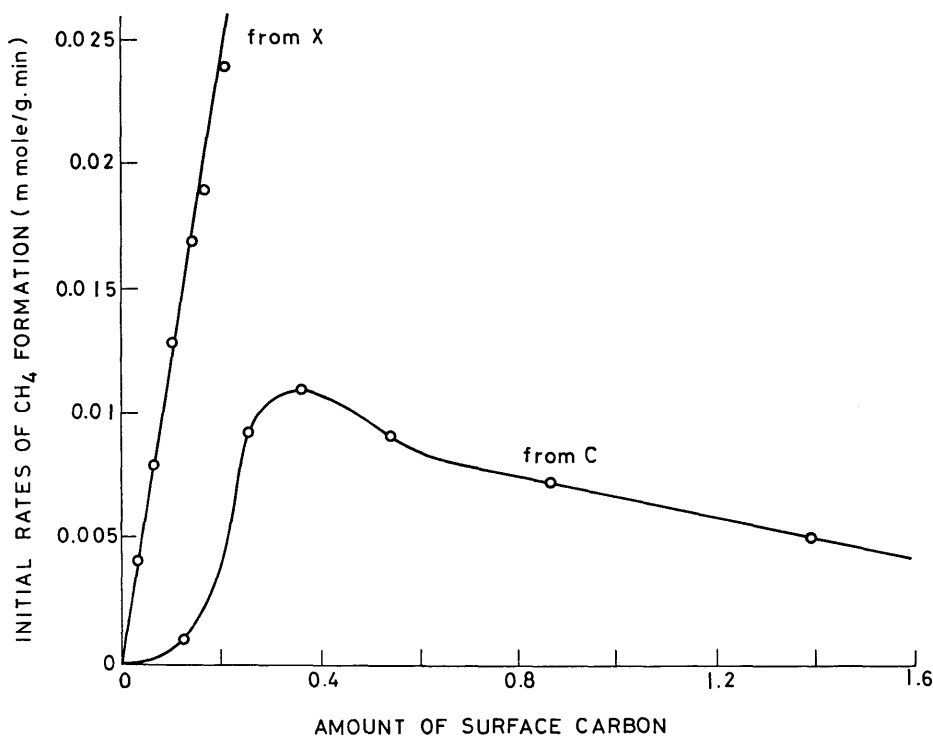
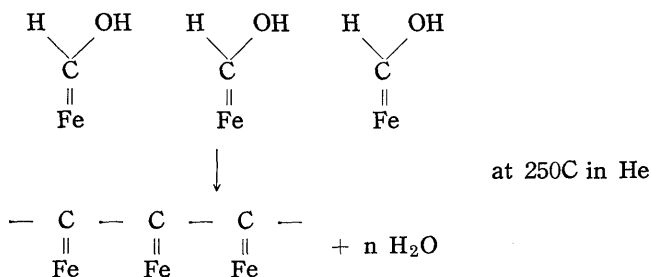


Fig. 7. Initial rates of methane formation by hydrogen flushing from the intermediate and from carbon on the surface



Accordingly, the deactivation of the surface intermediate could be estimated from the amount of water removed by the inert gas treatment. The resulting carbon species on the catalyst will have poor reactivity but it will be converted slowly to methane by hydrogen (Curve 7 in Fig. 3). In the presence of hydrogen, the intermediate is converted to methane and higher hydrocarbons (12). The hydrogenation of the intermediate to methane is expected to be much faster than the dehydration to the inactive carbon and water in the presence of hydrogen. However, the catalyst treated by helium over night which was assumed to contain no such complex still produced methane by hydrogen at a very low rate (Fig. 3) and the total amount of methane formation for this catalyst could not be neglected (Table 1). Araki and Ponec (9) suggested that the surface carbon played an important role for methanation on a nickel catalyst. Wentrick, Wood and Wise (8) reported in the similar system that the surface carbon was rapidly and quantitatively converted to methane on exposure of the catalyst to hydrogen. To check the reactivity of the carbon on the fused iron catalyst, the rate of hydrogenation was measured for the catalyst with various amounts of carbon on the surface. The results are shown in Fig. 6. In this experiment, the carbon covered catalyst was prepared by the disproportionation of carbon monoxide, and the hydrogenation of the carbon thus obtained was carried out by switching to hydrogen feed just as was done for the steady-state catalyst as described above. The initial rates of hydrogenation for various amounts of the surface carbon were obtained from the initial slopes of the curves in Fig. 6. These initial rates are plotted against the amount of surface carbon in Fig. 7. In this figure the rates of methane formed from the intermediate X, which is calculated from the results in Fig. 4, are also plotted against the amount of X for comparison. The rate of methane formation from the surface carbon first increased with increase of the amount, and the maximum rate of 0.01 mmole/g. min. was observed at 0.4 mmole/g. Further increase in the amount of carbon resulted in a decrease in the initial rate of hydrogenation to methane. This decrease of the rate is presumably due to the decrease of the surface sites available for hydrogen adsorption. On the other hand, the rate of methane formation from the intermediate complex X increased proportionally to the increase of its amount. The striking difference in the rate of hydrogenation between of the intermediate complex and of the surface carbon suggests that the effective reaction intermediate on the fused iron catalyst is not the surface carbon but the enol type complex.

The hydrogenation of the carbon formed on the surface by the disproportionation of carbon monoxide gave methane as the only hydrocarbon product, whereas the similar

hydrogenation of X gave small but definite quantities of ethane and propane. Whatever role the surface carbon may play in methane production, it is probably not active in chain building on the surface of the iron catalyst.

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